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INFLUENCE OF OPHIOLITIC ROCKS ON THE SPATIAL DISTRIBUTION OF CHROMIUM AND NICKEL IN STREAM SEDIMENTS OF THE CECINA RIVER BASIN (TUSCANY, ITALY)

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ABSTRACT

The concentrations of Cr and Ni and other heavy metals (Cd, Cu, Pb, Zn) have been determined in stream sediments collected into the Cecina River basin (Tuscany, Italy) in order to evaluate Cr and Ni levels and their spatial distribution and origin. An *aqua regia* digestion coupled to ICP-MS analysis has been performed on the samples. The distribution of Cr and Ni concentration as a function of grain size was also investigated, comparing finer samples (< 63 μm) and coarse samples (< 2000 μm). In Possera Creek samples, a left tributary of the Cecina River, another sieve fraction (< 125 μm) was sampled. The high levels of Cr and Ni in the stream sediments often exceed the thresholds of the Italian law currently in force (Legislative Decree No. 152/2006). Multivariate data analysis techniques (Hierarchical Clustering Analysis, HCA) were used to obtain information about the potential sources of heavy metals. The results indicate an Cr and Ni enrichment in stream sediments due to the presence of some extensive outcrops of serpentinized ultramafic rocks (ophiolites). The enrichment is major in the < 2000 μm fraction compared to the < 63 μm fraction.

INTRODUCTION

The trace elements Chromium (Cr) and Nickel (Ni) are heavy metals, an important group of environmental relevance due to their persistent and bioaccumulative nature (Beijer and Jernelöv, 1986; Andrews et al., 2004; Baird and Cann, 2004). Heavy metals occurrence in the natural environment are the result of discharges related to urban and industrial activity. They may also be of geological origin, i.e., supplied to the river system by weathering and erosion of heavy metals-bearing rocks (Zhang and Huang, 1993). Weathering of ultramafic rocks is known to produce soils and sediments with high Cr concentrations and other biologically toxic trace elements including Ni (Brooks, 1987; Schreier et al., 1987; Alexander et al., 1989; Gough et al., 1989; Gasser and Dahlgren, 1994; Oze et al., 2003; Mills et al., 2011; Kelepertzis et al., 2013).

The Cecina River basin (Tuscany, Italy) is an example of an area where there are many natural and anthropogenic sources of heavy metals. More specifically, in this catchment several ultramafic rocks, representing potential sources of some trace elements, are cropping out (Sorrentino, 2005; Franceschini and Laterza, 2010).

In this area several studies investigated the presence of hexavalent chromium in groundwater and the potential sources of Cr anomaly in Cecina Valley ophiolites (ARPAT, 2005; ARPAT, ICRAM, 2006; ARPAT, 2009; Righini et al., 2009; ARPAT, ICRAM, 2011; CNR, ARPAT, 2011; Lelli et al., 2013).

This paper reports the results of environmental characterization studies carried out by ARPAT (Environment Protection Agency - Tuscany Region) in Cecina River, Possera Creek and some tributaries.

The aim of the study is to contribute to the understanding of Cr and Ni distribution in the stream sediments of Cecina River basin related to a regional geological setting.

Cr AND Ni CONCENTRATIONS IN SEDIMENTS: NATURAL VERSUS ANTROPHOGENIC ORIGIN

Some heavy metals are essential for human life and plants but the concentrations of beneficial elements above a certain level may also create toxic effects (Adriano, 2001; Kaushik et al., 2009).

Chromium is a lithophile metallic element with an average upper continental crustal abundance of 85 mg/kg (Taylor and McLennan, 1985; Kabata-Pendias and Pendias, 2001; Rudnick and Gao, 2003). Cr is enriched in ultramafic rocks (1000-3000 mg/kg), along with Ni (2000 mg/kg) (Wedepohl, 1978; Mielke, 1979; Salminen et al., 2005). This metal is a major component of steel alloys and is used for steel coating as chrome plating. Chromates and dichromates containing Cr^{6+} are sometimes released into industrial effluents, especially from leather tanning and electroplating operations. Chromium, which was once thought to be nonessential, is yet known to have at least one important biological function (Frausto da Silva and Williams, 1991). It has a varying toxicity: soluble Cr^{3+} is considered relatively harmless, but Cr^{6+} is highly toxic, causing liver and kidney damage and acting as a carcinogen (WHO, 1996).

Nickel is a siderophile metallic element with chalcophilic and lithophilic affinities. It has an average upper continental crustal abundance of 50 mg/kg (Mielke, 1979; Taylor and McLennan, 1985). It is partitioned into ferromagnesian minerals such as olivine (up to 3000 mg/kg), orthopyroxene and spinel. Anthropogenic sources of Ni include fertilisers, steel works, metal plating and coinage, fuel combustion and detergents (Reimann and de Caritat, 1998). Nickel is considered essential for microorganisms and it has been implicated as having an essential role in human metabolism (McGrath, 1995). Most Ni^{2+} compounds are relatively non-toxic, but some compounds are highly toxic, and extreme excesses of

Ni are both toxic, causing dermatitis and gastric irritation, as well as carcinogenic illnesses (WHO, 1996).

Anthropogenic contamination of Cr end Ni are either associated with organic matter which is present in the thin fraction of sediments, or adsorbed on Fe/Mn hydrous oxides, or precipitated as hydroxides, sulphides and carbonates (Förstner, 1985). So they are more abundant in fine fraction of soils and stream sediments of industrial districts and represent an important indication of these activities (Schoer, 1985; Hlavay et al., 2004).

When interpreting spatial distribution of heavy metal concentrations, many controlling factors including surface geology, mineral deposits as well as anthropogenic activity must be taken into account (Kaushik et al., 2009). Heavy metals may be of geological origin and they come into the river system by weathering and erosion (Zhang and Huang, 1993). River sediments are an important environmental indicator of heavy metal pollution due to their ability to trace contamination sources (Jha et al., 1990; Gonçalves et al., 1992; Borovec, 1996; Soylak et al., 1996; Wardas et al., 1996; Soares et al., 1999). They may record both the current and the past discharges of heavy metals to the water system. However, the relative influence of natural and anthropogenic sources on the geochemistry of soils and sediments is not always clear, especially in areas where minerals contain high natural concentrations of heavy metals. The accumulation of heavy metals derived from both sources is controlled by the same processes of sediment transport and deposition (differential weathering, hydraulic sorting etc.). So it is difficult to determine the proportion of each source (Loring, 1991).

Therefore, for a better assessment of the environmental pollution process and for any soil management policy, it is important to be able to distinguish between chemical elements of natural and human origin.

STUDY AREA

The Cecina River is located in the central part of Tuscany. Its source is in the Metalliferous Hills at 1060 m a.s.l. The basin covers an area of 900 km² for a total length of 79 km². Its catchment extends mostly in the province of Pisa and, for a limited part, in the provinces of Siena and Grosseto. In its final segment, the Cecina River crosses the coastal plain in the province of Livorno to flow into the Tyrrhenian Sea near the town of Cecina (Fig. 1). The Cecina River has several tributaries, the main ones are: the Pavone, the Possera, the Trossa, the Rialdo, the Acquerta, and the Sterza Creeks (Fig 2a). Others tributaries considered in this work are the Cortolla, Santa Marta and Botrogrande Creeks. The Possera Creek on the left bank of Cecina River has a length of 18 km and flows across the Larderello geothermal field (Fig. 1b). The Cecina River has a marked torrential regime (flow rates measured on the middle course between 1.030 m^3/sec to 0.01 m^3/sec), with frequent phenomena of water stress. It presents flash or prolonged floods during rainy periods (from November to early spring) and a very low flow in summer.

The geology of the basin (Figs. 1 and 2b) is characterized by tectonic setting where sequences of deep marine clays, marls and Cretaceous to Eocene limestones (Ligurian Flysch Units) represent the sedimentary cover of the underlying Jurassic ophiolites (Mazzanti et al., 1961).

The ophiolites and their sedimentary cover are overlaid by Neogene sediments, which consist mainly of lacustrine clay at the bottom and marine clay at the top. The central-north area of the valley is characterized by Miocene and (above all) Pliocene sediments, referable to the Neogene complex (Bossio et al., 1996). The major extension of the Pliocene clays is around the Volterra area. The mid part of the Neogene sediments shows the occurrence of evaporites, represented by Messinian gypsum outcrops at the top and anhydrite and halite at the bottom (Testa and Lugli, 2000). The Neogene clayey formation (Argille Azzurre) are frequently interbedded with coarse-grained clastic deposits. Quaternary deposits form the fluvial and marine terraces of the main valley and of the coast.

Geothermal exploitation, industrial processing of boron and mining of halite from evaporite deposits are the most important activities that have contributed to the change of the Cecina Valley during the past century and making it a critical area (pilot river basin, EU Directive 2000/60/EC). These activities are concentrated in the area of Larderello, in

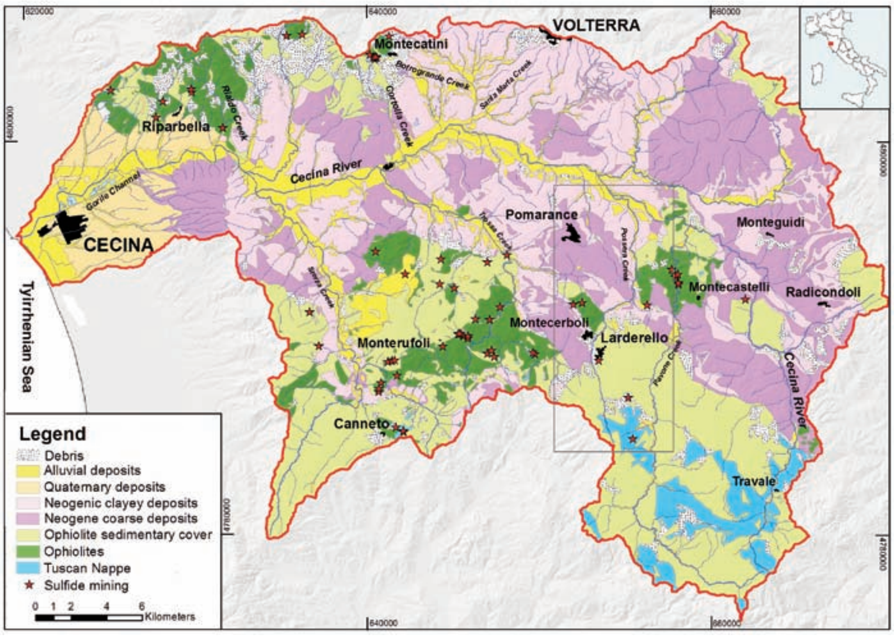


Fig. 1 - Geological sketch map of Cecina River basin.

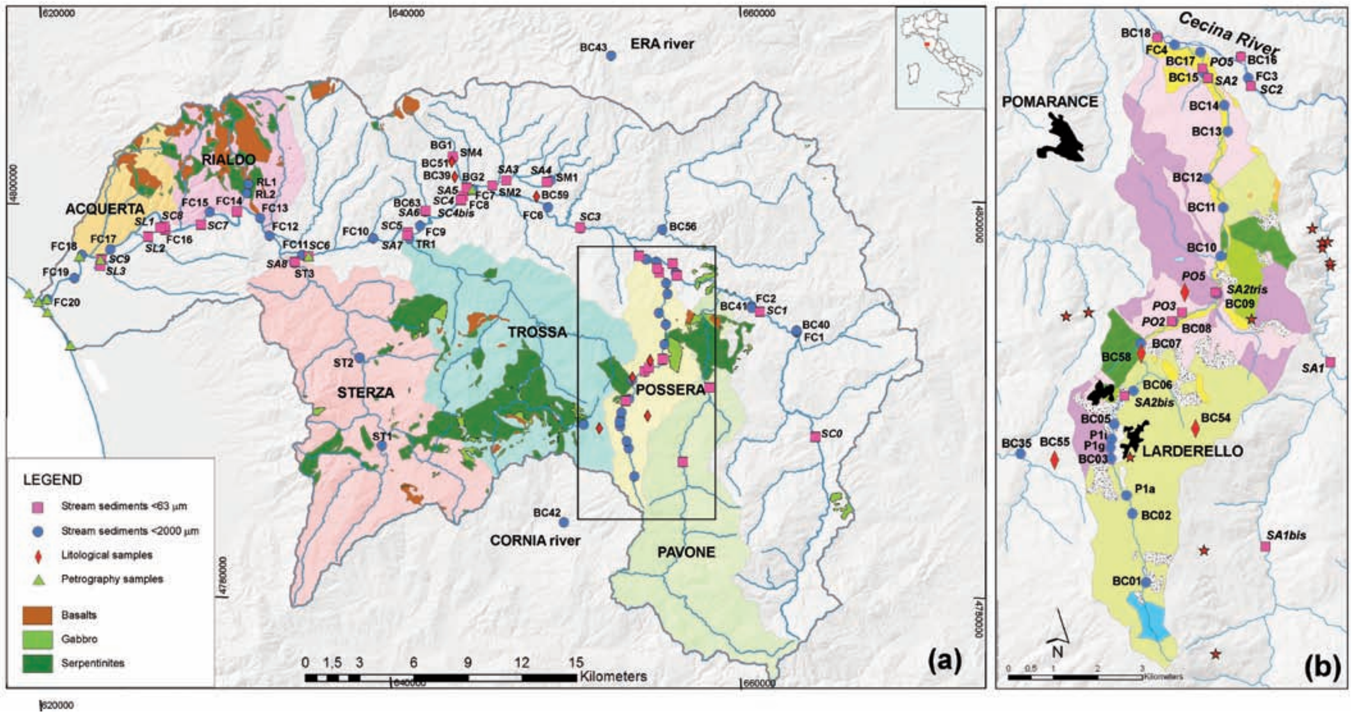


Fig. 2 - (a) Sketch map of Cecina River basin and sampling stations; the extension of sampled tributaries are reported. (b) In the focus Possera Creek catchment is shown (see Fig. 1 for geological legend).

the Possera catchment, and around the Botrogrande and Santa Marta catchments. Geothermal exhausted fluids and mud of industrial activities were released in the environment from 1913 to 1980 for the most part into the Possera Creek. Since 1980, the exhausted geothermal fluid from power production has been reinjected into the geothermal reservoir, and from 1975 onward the residual industrial mud has been disposed in a controlled landfill site (Grassi and Squarci, 2004). The other anthropogenic input are mining of mixed sulphide mineralization (Sb, Pb, Zn, Cu) associated with ophiolitic rocks. Near Montecatini Val di Cecina town was located the richest copper mine in Europe between 1827 and 1907. Many other small sulphide mining activities are present and they are always associated with ophiolitic outcrops (see Fig. 1).

Ophiolitic rocks in Cecina River basin

Ophiolite outcrops in Cecina River basin correspond to oceanic materials exhumed during the obduction phase of Apennine orogenesis. They testify to a compositionally heterogeneous lithosphere that includes mantle (serpentinized peridotite) and magmatic (basalt and gabbro) rocks. These outcrops in Northern Apennine are subdivided in Internal and External Ligurides, with lherzolitic and harzburgitic compositions respectively (Piccardo et al., 1990) and are affected by ocean floor metamorphism. The Liguride serpentinized peridotites represent early oceanization through passive litosphere extension of the Ligurian-Piedmontese Ocean spreading. (Tribuzio et al., 2000; Piccardo et al., 2002).

The ophiolites occurring in Cecina Valley belong to Internal Ligurides. The main outcrops in the area are localized around Riparbella, Monterufoli and Montecastelli. They are discontinuous outcrops, extended from Cecina to Volterra and characterized by abundance of serpentinite rocks. From outcrop to outcrop, the serpentinites may differ in deformation, fracturing and weathering. Large ophiolite slide blocks up to some hundreds meters long are also found within the flysch sequence as boudinaged olistoliths (Mazzanti, 1966; Abbate et al., 1980). Ophiolites in Cecina Valley are frequently affected by sulphide deposits linked to fossil hydrothermal alteration, remobilized by recent plutonic activity (Franceschini, 1993).

The serpentinized mantle rocks of Cecina Valley ophiolites and their related alteration products have high concentrations in Cr and Ni (Bini et al., 1990; Rumori et al., 2004) due to the presence in primary paragenesis of minerals such as Cr-spinel and Ni/Cr-rich pyroxenes (Tribuzio et al., 2004) and their corresponding secondary minerals (serpentine, Cr-chlorite etc.).

In Fig. 2a the distribution of the rocks belonging to ophiolitic suite (basalts, grabbro and serpentinites) and the subbasins extensions are reported (see also Table 1 about the spatial extension of ophiolitic rocks).

MATERIAL AND METHODS

Sampling

A total of 91 stream sediment samples were collected during summers 2005, 2008 and 2009 (sample location in Fig. 2).

In channel beds and depositional bars of the Cecina River and in some of its main tributaries 26 stream sediments samples were collected during summer 2005, using the transect sampling method (U.S.EPA, 2001). In the field, sample separation of the fractions < 63 µm has been carried out. In situ, surficial water was used for the wet-sieving of the sediment to minimize the loss of particulate-bound trace metals to the dissolved phase. The sieved fractions were recovered in polyethylene containers of 100 ml to be analyzed. The analytic results were reported in Table 3.

Using the same procedures during summers 2008 and

Table 1 - Extension of ophiolite outcrops in Cecina River basin and their distribution in main sub-basins.

	Area	*OPHIOLITES*		*basalts*		*gabbro*		*serpentinites*	
	sq. km	*sq. km*	*%*	*sq. km*	*%*	*sq. km*	*%*	*sq. km*	*%*
CECINA	**927**	**70.77**	**7.63**	**15.48**	**21.9**	**6.23**	**8.8**	**49.07**	**69.3**
ACQUERTA	23	3.79	16.5	2.48	65.4	0.05	1.3	1.26	33.3
PAVONE	89	5.48	6.2	0.40	7.2	0.57	10.4	4.51	82.3
POSSERA	36	3.20	8.9	0.07	2.2	1.17	36.7	1.95	61.1
RIALDO-LUPIA	45	16.32	36.3	7.96	48.8	0.02	0.1	8.34	51.1
TROSSA	112	25.25	22.5	1.67	6.6	2.05	8.1	21.53	85.3
STERZA	128	10.98	8.6	0.68	6.2	0.80	7.3	9.49	86.4
Sum sub-basins	**433**	**65.02**	**15.0**	**13.26**	**20.4**	**4.67**	**7.2**	**47.09**	**72.4**
Remainder	**494**	**5.75**	**1.2**	**2.22**	**38.6**	**1.56**	**27.1**	**1.98**	**34.4**

2009, the fraction < 2000 µm of 38 stream sediment samples from Cecina River and its main tributaries were taken (Table 2).

Grain size distribution was measured in situ on 16 samples of the Possera Creek and 3 samples of Cecina River (Fig. 2) by wet sieving. For these samples the following three fractions were separated: silt+clay (< 63 µm), fine sand (63 µm < × < 125 µm) and sand (125 µm < × < 2000 µm). The three fractions were analyzed separately in order to compare the amounts of heavy metals accumulated in each particle sizes (Table 4). The Table 2 shows the results of the chemical analysis on fraction < 2000 µm corrected with respect to the percentages of the different particle sizes.

Sampling has also covered the main geological formations presents in the surveyed area, for a total of 7 samples (Table 5). Among these, the sample BC58 represents a residual soil on serpentinite.

Analytical methods

The technique of the pseudo-total digestion has been used (SW-846 EPA Method 3051A, 1998). The samples were dried at 30°C for 24 h. About 10 g of sample was pulverized and sieved of 200 µm mesh when necessary. Therefore about 0.3 g of powdered sample was digested by a closed-digestion procedure in inverse *aqua regia* (9 ml HNO_3 65% and 3 ml HCl 37%). A microwave system was used to accomplish sediment digestion (SW-846 EPA Method 3051A, 1998; Sandroni et al., 2003). A blank was prepared with the same amount of acids for each digestion program. After cooling, the resulting solutions were diluted to 50 ml in volumetric flasks with MilliQ water (18.2 MΩ cm). Some sediment samples were analyzed in duplicates (RSD%: Cd = 4.8210, Cr = 5.7596, Cu = 4.6168, Ni = 5.9113, Pb = 6.0837, Zn = 5.1428).

After pseudo-total digestion of samples, metal concentrations (Cd, Cr, Cu, Ni, Pb, Zn) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), using Varian Vista-MPX instrument and following Apha Awwa WEF Standard Metod 3120/2005. The analyses were performed by the laboratory of the ARPAT, Department of Pisa.

The accuracy of the analytical procedures have been checked by analysing a multistandard NIST traceable certificate (Recovery %: Cd = 97.0, Cr = 95.2, Cu = 101.0, Ni = 103.8, Pb = 97.5, Zn = 99.4).

In addition to chemical analyses, petrographic thin sections on granulometric range between 2000 µm and 63 µm of Cecina River selected samples (SC4, SC5, SC6, SC9, Cf1, FO1, FO4) and some sand samples from the lateral beaches (Ssc, Snc, Cm1) were investigated using optical microscopy. To prepare thin sections, each sand sample is mixed with epoxy and allowed to set into a small block. Once the blocks harden, they are treated as rocks and thin sectioned. Polished thin sections were used for standard light microscope observation.

Elaboration of results

Experimental data have been elaborated by multivariate statistical analysis using the software STATISTICA ® (StatSoft Inc., Tulsa, OK, USA). The Hierarchical Clustering Analysis (HCA) of raw data was applied. Complete Linkage as cluster analysis and Pearson correlation as similarity measure was used.

RESULTS

Heavy Metal concentrations

Data of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) determination in fraction < 2000 µm and in fraction < 63 µm are presented in Table 2 and Table 3 respectively, with the main statistical indices.

The average Cr and Ni content in the fraction < 2000 µm of stream sediments collected in Cecina catchment are respectively 307 mg/kg and 366 mg/kg, and in the fraction < 63 µm 109 mg/kg and 150 mg/kg. The maximum Cr values are in samples BC16 (fraction < 2000 µm, value 998.3 mg/kg) and BC11 (fraction < 63 µm, value 236 mg/kg). Ni presents the maximum values in samples RL2 (fraction < 2000 µm, value 1006 mg/kg) and in FC 14 (fraction < 63µm, value 337.3 mg/kg).

The concentration of 58 mg/kg is the minimum value found for Cr (sample FC1) and Ni (sample BC42) in fraction < 2000 µm (Table 2). In fraction < 63 µm (Table 3) the minimum value of Cr (19.2 mg/kg) and Ni (29.2 mg/kg) is found in the sample SA8.

Table 6 shows the main statistical indices of the analyzed metals according to the particle size and to the sampled watercourse (Cecina River, Possera Creek, other tributaries). The term “no Ophiolite” refers to a group of samples taken into sub-basins (Botro St. Marta, Cortolla, Fosci) or in external catchments (Era and Cornia basins) where the ophiolitic outcrops are missing. The main statistical indices of seven rock samples are also reported.

Table 2 - Metal concentrations (mg/kg dry weight) in fraction < 2000 µm of Cecina River samples and of some its tributary.

	Code	*Stream*	*Locality*	*est 32T UTM*	*nord*	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
Cecina river	**FC 20**	Cecina	Marina	621153	4795635	0.02	899.8	46.3	665.9	12.0	54.0
	FC 19	Cecina	Aurelia	622627	4796826	0.10	769.2	125.5	379.4	16.9	69.5
	FC 18	Cecina	Niccolai	623058	4798121	0.09	137.6	135.8	503.8	16.9	67.4
	FC 17	Cecina	Acquerta	624636	4798433	0.08	154.3	133.6	522.4	12.9	73.4
	FC 16	Cecina	Steccaia	627643	4799714	0.10	176.2	149.3	715.7	12.6	64.1
	FC 15	Cecina	Mandracce	630144	4800503	0.05	151.9	86.6	622.9	10.6	55.2
	FC 14	Cecina	Melatina	631632	4800517	0.08	233.4	122.3	641.3	7.8	55.5
	FC 13	Cecina	S.Antonio	632927	4800175	0.05	223.3	33.3	724.3	3.1	39.5
	FC 12	Cecina	Lupicaia	633463	4799178	0.06	223.7	14.2	488.4	9.0	47.7
	FC 11	Cecina	Casino di terra	635264	4798121	0.06	234.9	17.2	715.8	9.4	45.6
	FC 10	Cecina	Turbone	639194	4799044	0.08	395.0	78.6	504.6	10.6	71.8
	FC 9	Cecina	Ponteginori	641784	4799729	0.06	696.5	84.3	735.6	10.7	68.0
	FC 7	Cecina	Montegemoli	644717	4801768	0.08	175.4	15.7	372.3	12.1	62.5
	FC 6	Cecina	San Lorenzo	648870	4800756	0.13	144.4	21.5	287.6	17.0	80.2
	BC59	Cecina	Ponte di Ferro	650671	4799595	0.60	532.9	20.9	371.1	10.1	72.7
	BC18	Cecina	Possera downstream	654305	4797888	0.50	817.5	27.0	336.0	11.9	91.6
	FC 4	Cecina	Possera downstream	653916	4798061	0.05	225.8	18.3	819.4	8.5	48.9
	BC16	Cecina	Possera upstream	655960	4797150	0.59	998.3	25.3	498.6	9.6	80.5
	FC 3	Cecina	Berignone	655792	4797630	0.09	155.4	26.4	356.9	19.3	63.8
	FC 2	Cecina	Pian di Goro	660136	4795273	0.14	121.7	33.5	228.2	22.2	96.8
	BC41	Cecina	Ponte Spineta	660176	4795174	0.60	207.3	27.5	173.9	15.0	85.7
	BC40	Cecina	Radicondoli	662654	4793825	0.80	131.8	27.5	101.9	16.5	96.1
	FC 1	Cecina	Radicondoli	662639	4793919	0.13	58.0	33.9	75.4	23.8	92.4
Possera creek	**BC01**	Possera	Castelnuovo	653656	4785873	0.53	79.9	60.0	88.4	34.1	142.5
	BC02	Possera	Bagno al Morbo	653361	4787415	0.78	82.3	58.3	103.3	30.8	163.3
	P1a	Possera	Tunnel upstream	653226	4787821	0.70	106.0	59.0	125.0	28.0	154.0
	BC03	Possera	Larderello Tunnel	652875	4788644	3.17	170.5	53.8	138.5	30.6	181.9
	P1i	Possera	Larderello SCL	652891	4789071	1.00	86.0	57.0	125.0	210.0	149.0
	P1g	Possera	Larderello Enel	652860	4788890	0.80	68.0	57.0	102.0	22.0	133.0
	BC05	Possera	Idros station	652945	4789413	1.06	123.5	50.3	140.9	52.6	175.7
	BC06	Possera	Montecerboli	653380	4790162	1.15	220.7	422.5	195.9	423.6	210.9
	BC07	Possera	Centrale Gabbro	653544	4791210	0.96	178.3	70.7	164.6	40.3	165.0
	BC08	Possera	Bulera upstream	654274	4791693	0.80	262.8	39.4	262.0	21.5	130.0
	BC09	Possera	Bulera downstream	655255	4792319	0.71	308.0	30.1	282.7	18.9	103.2
	BC10	Possera	Palagione	655340	4793163	0.71	315.1	27.0	334.7	11.9	66.7
	BC11	Possera	Podere Citerna	655395	4794249	0.40	650.2	29.0	374.8	10.8	92.6
	BC12	Possera	Sodolungo	655030	4794901	0.50	148.8	31.0	169.2	19.5	84.4
	BC13	Possera	Podernuovo	655498	4795954	0.49	505.2	28.9	419.2	16.1	72.3
	BC14	Possera	Santa Lina	655418	4796541	0.59	290.5	31.5	302.2	30.0	81.3
	BC15	Possera	Concrete bridge	654951	4797268	0.49	289.8	28.7	266.8	13.6	87.5
	BC17	Possera	Conoide	654886	4797732	0.49	292.0	26.2	244.6	15.4	85.5
Others	**RL1**	Rialdo	Querry upstream	632185	4801545	0.30	544.0	112.0	583.0	7.8	80.0
	RL2	Rialdo	Molino di Rialdo	632290	4802055	0.10	664.0	70.0	1006.0	<5	50.0
	ST1	Sterza	Casotto	639670	4787578	0.11	415.6	101.7	540.6	15.4	80.9
	ST2	Sterza	Gabella	638433	4792428	0.09	848.3	71.5	742.4	10.9	62.5
	ST3	Sterza	Guardistallo	634838	4797672	0.09	632.7	75.3	621.5	15.4	69.6
	TR1	Trossa	Ponteginori	641191	4799015	0.06	447.8	76.4	806.6	7.4	60.8
	BC35	Trossa	Secolo Creek	650847	4788751	0.80	198.0	39.0	202.0	21.0	143.0
	BG1	Botrogrande	Buriano	643627	4804030	0.11	180.5	166.6	302.4	25.2	118.8
	BG2	Botrogrande	Solvay	644898	4803667	0.81	220.7	3044.7	143.2	17.5	277.8
no Ophiolite	**SM 1**	Santa Marta	Poppiano	649033	4803495	0.11	92.5	75.7	165.8	26.5	85.2
	SM 2	Santa Marta	Saline	646548	4802259	0.44	239.4	169.0	254.3	51.7	220.7
	BC56	Fosci	Intersection	655218	4799512	<0,5	103.0	17.0	90.0	8.7	48.0
	BC63	Cortolla	Castelluccio	642077	4800521	0.20	104.0	8.4	95.0	3.6	25.0
	BC42	Cornia	Leccia	649759	4783323	0.80	77.0	45.7	58.0	16.4	133.0
	BC43	Era	Volterra	652375	4809171	0.30	397.0	13.0	203.0	8.6	45.0
					Mean	**0.4**	**307**	**119**	**366**	**29**	**96**
					SD	**0.5**	**241**	**407**	**239**	**62**	**51**
					Max	**3.2**	**998**	**3045**	**1006**	**424**	**278**
					Min	**<0.5**	**58**	**8**	**58**	**3**	**25**

The concentrations of Possera Creek samples were corrected with respect to the percentages of the different particle sizes, see Table 4.

Table 3 - Metal concentrations (mg/kg dry weight) in fraction < 63 μm of Cecina River samples and of some its tributary.

	Code	*Stream*	Locality	*est* *32T UTM*	*nord*	Cd	Cr	Cu	Ni	Pb	Zn
Cecina	**SC0**	**Cecina**	Anqua	663690	4788070	0.20	73.0	36.0	102.0	29.0	94.0
	BC41	**Cecina**	Ponte Spineta	660176	4795174	0.60	145.0	38.1	187.0	15.5	98.0
	SC1	**Cecina**	Monteguidi	660611	4794976	<0,05	205.8	31.6	265.3	19.8	63.3
	SC2	**Cecina**	Berignone	656020	4796974	<0,05	117.4	33.5	140.6	14.9	76.3
	FC3	**Cecina**	Berignone	655792	4797630	0.21	125.8	106.6	213.1	19.3	106.3
	FC4	**Cecina**	Possera downstream	653916	4798061	0.18	65.2	42.1	207.1	32.3	114.1
	BC16	**Cecina**	Possera upstream	655960	4797150	0.50	127.0	48.1	117.0	18.3	105.0
	BC18	**Cecina**	Possera downstream	654305	4797888	0.50	167.0	34.0	136.0	15.2	91.2
	SC3	**Cecina**	Ponte di Ferro	650661	4799640	<0,05	156.5	36.8	263.3	18.1	89.1
	BC59	**Cecina**	Ponte di Ferro	650671	4799595	0.60	119.0	38.0	108.0	15.9	109.0
	SC4	**Cecina**	Montegemoli	645794	4801970	0.30	88.0	34.0	113.0	29.0	87.0
	SC4bis	**Cecina**	Cacciatina	644176	4801371	<0.05	92.0	35.0	112.0	25.0	85.0
	FC8	**Cecina**	Cacciatina	644047	4801172	0.14	74.0	118.2	151.3	17.3	119.8
	SC5	**Cecina**	Ponteginori	641114	4799375	<0.05	121.0	36.8	144.6	21.5	81.9
	SC6	**Cecina**	Sterza	635617	4798052	<0.05	172.4	34.3	281.2	28.3	122.7
	FC14	**Cecina**	Melatina	631632	4800517	0.12	95.6	64.2	337.3	43.6	91.2
	SC7	**Cecina**	S.Martino	629655	4799809	<0.05	75.7	25.2	114.5	18.5	56.2
	SC8	**Cecina**	Steccaia upstream	627679	4799528	0.10	128.0	39.0	206.0	13.0	71.0
	SC8bis	**Cecina**	Steccaia downstream	627647	4799724	0.10	152.0	38.0	234.0	14.0	72.0
	SL1	**Cecina**	Gorile channel high	627395	4799633	0.10	105.0	22.0	158.0	13.0	48.0
	SL2	**Cecina**	Gorile channel medium	626731	4799138	0.10	153.0	21.0	222.0	11.0	42.0
	SL3	**Cecina**	Gorile channel down	624090	4797532	0.20	91.0	30.0	153.0	41.0	85.0
	SC9	**Cecina**	Aurelia	624140	4797869	<0.05	206.0	44.0	244.0	24.0	90.0
Possera	**PO2**	**Possera**	Bulera upstream	654243	4791705	0.31	66.9	154.1	128.3	27.7	118.9
	PO3	**Possera**	Bulera	654467	4791899	0.09	155.7	114.3	218.4	23.5	125.7
	PO5	**Possera**	Conoide	654928	4797377	0.12	54.6	104.9	186.6	16.5	103.3
	SA2	**Possera**	Cecina river	655055	4797150	<0.05	94.7	38.3	112.2	21.4	84.3
	SA2bis	**Possera**	Larderello	653174	4790054	0.80	87.3	77.1	122.7	85.8	176.4
	SA2tris	**Possera**	S.Dalmazio	655227	4792354	0.50	75.7	34.9	93.6	21.1	90.9
	BC01	**Possera**	Castelnuovo	653656	4785873	0.40	59.9	81.4	55.8	37.9	124.0
	BC02	**Possera**	Bagno al Morbo	653361	4787415	0.70	73.3	95.4	65.2	36.0	170.0
	BC03	**Possera**	Down tunnel	652875	4788644	1.30	69.8	87.2	83.8	45.2	290.0
	BC05	**Possera**	Idros station	652945	4789413	0.80	89.2	75.7	84.2	47.0	193.0
	BC06	**Possera**	Montecerboli	653380	4790162	0.90	109.0	136.0	102.0	108.0	219.0
	BC07	**Possera**	Centrale Gabbro	653544	4791210	0.80	57.8	77.9	69.7	41.6	166.0
	BC08	**Possera**	Bulera upstream	654274	4791693	0.80	76.9	55.8	86.2	28.7	129.0
	BC09	**Possera**	Bulera downstream	655255	4792319	0.80	109.0	44.1	116.0	23.1	125.0
	BC10	**Possera**	Palagione	655340	4793163	0.80	160.0	51.7	188.0	23.0	105.0
	BC11	**Possera**	Podere Citerna	655395	4794249	0.40	236.0	42.2	321.0	15.8	116.0
	BC12	**Possera**	Sodolungo	655030	4794901	0.50	140.0	37.9	169.0	22.3	105.0
	BC13	**Possera**	Podernuovo	655498	4795954	0.40	102.0	36.3	110.0	15.2	86.2
	BC14	**Possera**	Santa Lina	655418	4796541	0.50	130.0	35.9	137.0	17.2	100.0
	BC15	**Possera**	Concrete bridge	654951	4797268	0.40	107.0	33.5	101.0	14.7	98.6
	BC17	**Possera**	Conoide	654886	4797732	0.40	123.0	30.6	158.0	16.0	90.0
Others	**SA1**	**Pavone**	Montecastelli	657803	4790796	0.10	56.5	15.2	51.5	12.2	40.5
	SA1bis	**Pavone**	Castelnuovo	656348	4786675	0.70	78.8	33.1	106.9	15.7	87.3
	SA4	**Santa Marta**	Saline	645794	4801970	0.11	80.0	49.0	104.0	50.0	118.0
	SA3	**Santa Marta**	Saline upstream	648824	4802159	<0.05	60.0	48.0	74.0	42.0	88.0
	SM2	**Santa Marta**	Saline	646548	4802259	0.49	76.9	217.4	169.4	42.0	225.6
	SA5	**Botrogrande**	Botro Grande Creek	644371	4801847	<0.05	94.8	127.4	97.9	16.7	125.9
	SM4	**Botrogrande**	Buriano	643605	4803587	0.11	58.3	202.5	149.6	15.7	100.8
	SA6	**Cortolla**	Castelluccio	642093	4800567	<0,05	102.4	37.1	122.1	18.2	78.1
	SA7	**Trossa**	Ponteginori	641070	4799221	<0.05	232.1	36.1	271.7	12.6	32.6
	SA8	**Sterza**	Guardistallo	634852	4797732	<0.05	19.2	20.8	29.2	14.9	55.1
					Mean	**0.4**	**109**	**60**	**150**	**26**	**107**
					SD	**0.3**	**46**	**44**	**70**	**18**	**47**
					Max	**1.3**	**236**	**217**	**337**	**108**	**290**
					Min	**<0.05**	**19**	**15**	**29**	**11**	**33**

Table 4 - Grain size distribution and concentrations (mg/kg dry weight) in stream sediments collected during summer 2008.

Code	*Locality*	*Grain-size (%)*			*Cd*			*Cr*			*Cu*			*Ni*			*Pb*			*Zn*		
	size in mm	<63	63-125	125-2000	2000-125	125-63	<63	2000-125	125-63	<63	2000-125	125-63	<63	2000-125	125-63	<63	2000-125	125-63	<63	2000-125	125-63	<63
BC01	Castelnuovo	33	4	63	0.6	0.4	0.40	92.7	46.2	59.9	47.1	83.2	81.4	108.0	54.3	55.8	30.3	60.5	37.9	153.0	132.0	124.0
BC02	Bagno al Morbo	13	4	83	0.8	0.7	0.70	84.7	61.0	73.3	51.2	87.9	95.4	111.0	65.3	65.2	29.7	37.6	36.0	162.0	168.0	170.0
BC03	Down tunnel	9	2	89	3.4	0.9	1.30	182.0	93.3	69.8	49.6	98.7	87.2	145.0	85.4	83.8	28.8	49.5	45.2	168.0	354.0	290.0
BC05	Idros station	11	3	86	1.1	0.9	0.80	129.0	88.2	89.2	46.0	83.9	75.7	150.0	79.0	84.2	53.6	43.8	47.0	173.0	191.0	193.0
BC06	Montecerboli	13	4	83	1.2	0.9	0.90	244.0	111.0	109.0	483.0	131.0	136.0	215.0	113.0	102.0	490.0	105.0	108.0	209.0	222.0	219.0
BC07	Centrale Gabbro	17	3	79	1.0	0.9	0.80	209.0	72.7	57.8	66.6	131.0	77.9	189.0	76.9	69.7	39.5	53.6	41.6	163.0	209.0	166.0
BC08	Bulera upstream	7	4	89	0.8	0.8	0.80	286.0	74.7	76.9	37.3	56.4	55.8	284.0	83.2	86.2	20.7	26.1	28.7	130.0	132.0	129.0
BC09	Bulera downstream	11	2	87	0.7	0.7	0.80	337.0	112.0	109.0	27.9	49.8	44.1	307.0	119.0	116.0	18.3	24.6	23.1	100.0	124.0	125.0
BC10	Palagione	7	3	90	0.7	0.8	0.80	332.0	183.0	160.0	24.1	54.6	51.7	351.0	202.0	188.0	10.6	22.5	23.0	62.7	95.2	105.0
BC11	Podere Citerna	17	4	79	0.4	0.4	0.40	760.0	193.0	236.0	25.5	43.8	42.2	394.0	206.0	321.0	9.6	14.8	15.8	87.5	93.3	116.0
BC12	Sodolungo	16	5	79	0.5	0.5	0.50	151.0	142.0	140.0	28.9	42.5	37.9	169.0	173.0	169.0	18.8	22.2	22.3	78.9	103.0	105.0
BC13	Podernuovo	7	0	93	0.5	0.4	0.40	535.0	120.0	102.0	28.3	47.2	36.3	442.0	130.0	110.0	16.2	19.3	15.2	71.2	102.0	86.2
BC14	Santa Lina	6	6	88	0.6	0.5	0.50	314.0	116.0	130.0	31.0	33.9	35.9	326.0	128.0	137.0	31.9	15.5	17.2	79.3	91.7	100.0
BC15	Concrete bridge	12	2	86	0.5	0.4	0.40	320.0	91.9	107.0	28.1	27.8	33.5	294.0	92.7	101.0	13.4	13.6	14.7	86.1	83.8	98.6
BC16	Possera upstream	5	2	93	0.6	0.5	0.50	1061.0	107.0	127.0	23.8	43.3	48.1	526.0	110.0	117.0	9.0	16.1	18.3	78.8	98.6	105.0
BC17	Conoide	7	3	90	0.5	0.4	0.40	311.0	130.0	123.0	25.7	31.0	30.6	256.0	113.0	158.0	15.3	17.1	16.0	84.9	91.0	90.0
BC18	Possera downstream	11	2	88	0.5	0.5	0.50	911.0	118.0	167.0	26.0	33.8	34.0	365.0	107.0	136.0	11.4	15.1	15.2	91.7	88.9	91.2
BC59	Ponte di Ferro	4	1	94	0.6	0.6	0.60	558.0	123.0	119.0	19.9	37.3	38.0	387.0	113.0	108.0	9.7	15.8	15.9	70.5	105.0	109.0
BC41	Ponte Spineta	7	5	88	0.6	0.6	0.60	218.0	117.0	145.0	26.4	33.1	38.1	177.0	111.0	187.0	15.0	15.5	15.5	84.9	87.0	98.0

Samples were collected in Possera Creek except the last three, taken in the Cecina River.

In the Cecina River the stream sediments < 2000 µm have average Cr value of 342±287 mg/kg and Ni average of 471±214 mg/kg (Table 6). The average Cr value in Possera Creek stream sediments < 2000 µm is 232±155 mg/kg. These samples show an average Ni concentration of 213±101 mg/kg. The other tributaries are characterized by higher concentrations of these two heavy metals (average of Cr = 461 mg/kg and Ni = 550 mg/kg). Where ophiolitic outcrops are missing, samples (define "no Ophiolite" in Table 6) show relatively lower contents of Cr and Ni (average of 169 and 144 mg/kg, respectively). Only the samples BC43 and SM2 differ from this trend (respectively Cr 397 mg/kg and Ni 203 mg/kg; Cr 239.4 mg/kg and Ni 254.3 mg/kg in Table 2).

The average Cr content in the stream sediments fraction < 63 µm of Cecina River is 124±42 mg/kg and the Ni average is 186±66 mg/kg. The stream sediments < 63 µm of Possera Creek have average Cr value of 107±43 mg/kg and Ni average of 121±61 mg/kg. Other tributaries have Cr average of 91±59 mg/kg and Ni average of 108±69 mg/kg.

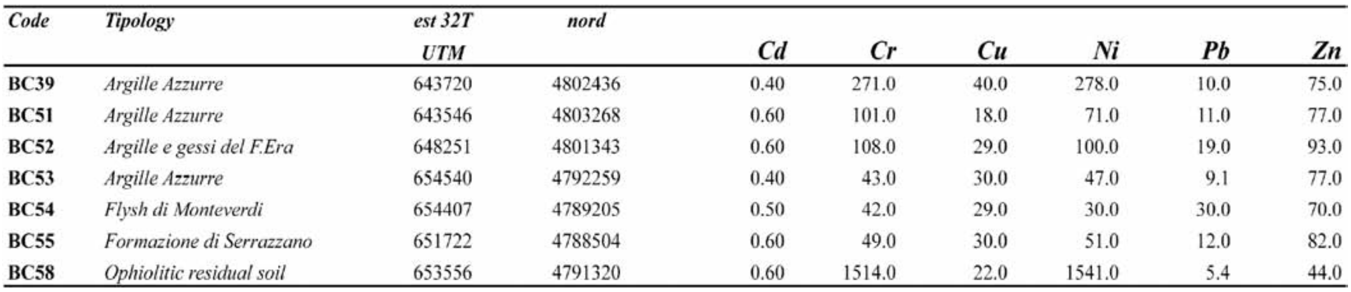
Among other heavy metals analyzed (Cd, Cu, Pb, Zn), the Cd has an average value of 0.9±0.6mg/kg in samples < 2000 µm of Possera Creek, while for other watercourses the average value is < 0.4 mg/kg (Table 6). This metal presents an average of 0.7±0.2 mg/kg in fraction < 63 µm of Possera Creek; the average concentration in the other watercourses is < 0.2 mg/kg. Maximum values of this metal are observed in the sample BC03 of Possera Creek collected near Larderello (3.17 mg/kg in fraction < 2000 µm see Table 2; 1.3 mg/kg in the fraction < 63 µm see Table 3). The average abundance of Cd observed in the lithological samples is 0.5±0.1 mg/kg (Table 6) and variable within a narrow range (0.4 mg/kg - 0.6 mg/kg).

The average Cu concentration in coarse fraction is 57±46 mg/kg in Cecina River samples and 64 ±91 mg/kg in Possera Creek samples, but the maximum value of the metal is observed in BG 2 (3044.7 mg/kg), sample taken in the Botrogrande Creek (Table 2). In coarse fraction of the other watercourses ("Others" in Table 6) the average Cu value is 417±986 mg/kg. In the fine fraction the average content of the metal is 60±28 mg/kg in samples of Possera Creek and for Cecina River and other watercourse < 45 mg/kg. The maximum value of 217.4 mg/kg is found in the sample of Santa Marta Creek (SM2) but high Cu values are also observed in the stream sediments of the Botrogrande Creek (SA5, SM4). In rock samples, the Cu content is variable between a minimum of 18 mg/kg and a maximum of 40 mg/kg (BC51 and BC39 samples of the Argille Azzurre, see Table 5), with an average content of 28 mg/kg.

The fraction < 2000 µm of Possera Creek stream sediments has an average Pb content of 57±102 mg/kg and in the sample BC06 of this watercourse is observed the maximum of concentration metal (423.6 mg/kg).

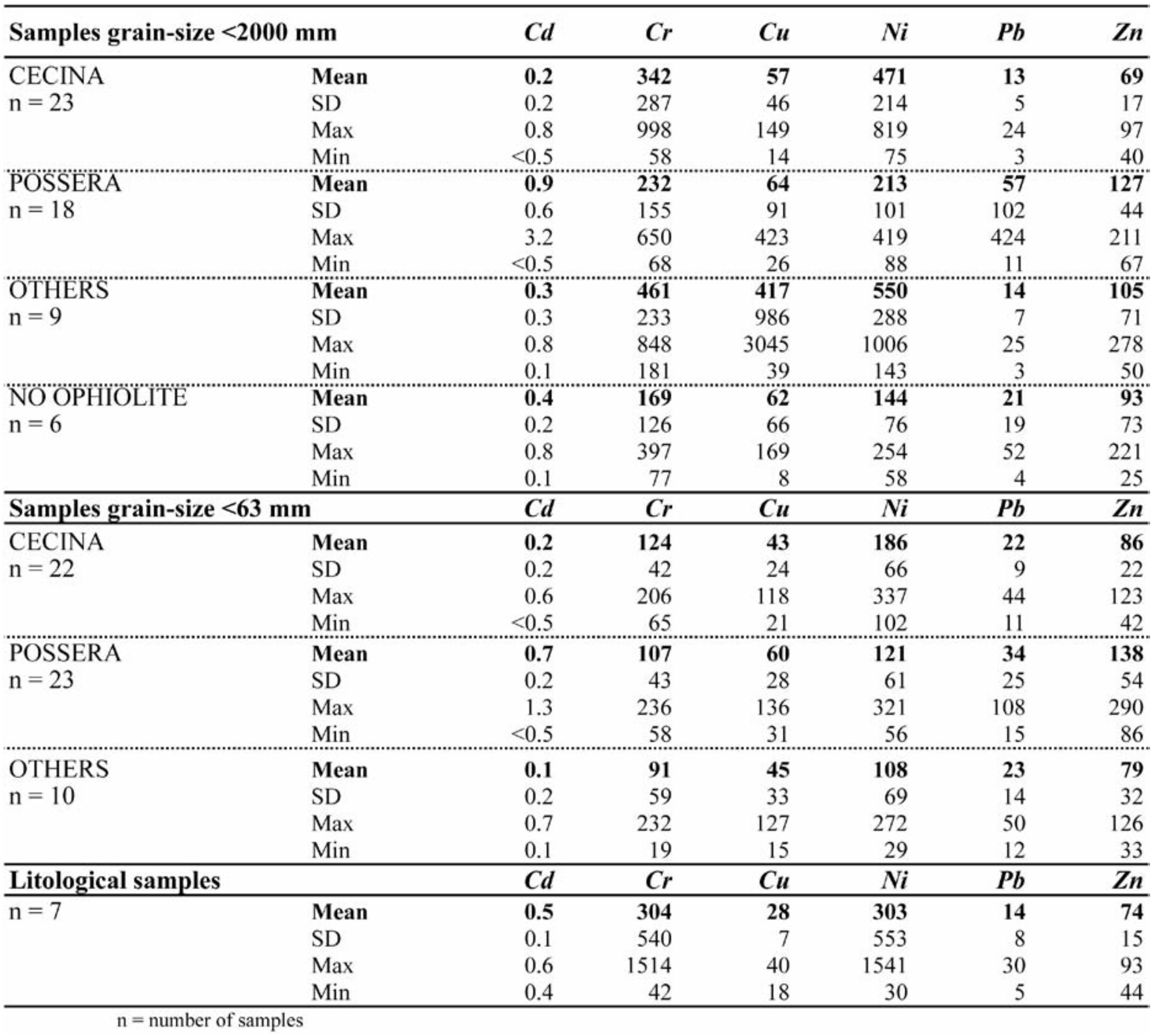
The Cecina River and the other watercourse have an average Pb content of 13 mg/kg and 14 mg/kg respectively, while the stream sediments sampled in the basins not affected by ophiolitic outcrops ("no Ophiolite" in Table 6) present an average of 21±19 mg/kg. The average Pb level is 34±25 mg/kg in the fine fraction of the Possera Creek, 22±9 mg/kg in the Cecina River and 23±14 mg/kg in other streams. The maximum value in this fraction (108 mg/kg) is found in the BC06 sample of Possera Creek, as well as for the coarse fraction. The lithology of the investigated area has an average Pb value of 14±8 mg/kg; the sample of Flysh di Monteverdi (BC54) has the highest content (30 mg/kg in Table 5) and the minimum of 5.4 mg/kg is found in ophiolitic soil (BC58).

Table 5 - Metal concentrations (mg/kg dry weight) in lithological samples of Cecina River basin.



Code	*Tipology*	*est 32T UTM*	*nord*	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
BC39	*Argille Azzurre*	643720	4802436	0.40	271.0	40.0	278.0	10.0	75.0
BC51	*Argille Azzurre*	643546	4803268	0.60	101.0	18.0	71.0	11.0	77.0
BC52	*Argille e gessi del F.Era*	648251	4801343	0.60	108.0	29.0	100.0	19.0	93.0
BC53	*Argille Azzurre*	654540	4792259	0.40	43.0	30.0	47.0	9.1	77.0
BC54	*Flysh di Monteverdi*	654407	4789205	0.50	42.0	29.0	30.0	30.0	70.0
BC55	*Formazione di Serrazzano*	651722	4788504	0.60	49.0	30.0	51.0	12.0	82.0
BC58	*Ophiolitic residual soil*	653556	4791320	0.60	1514.0	22.0	1541.0	5.4	44.0

Table 6 - Summary statistics of metal concentrations (mg/kg dry weight) in the main samples groups.



Samples grain-size <2000 mm		*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
CECINA n = 23	**Mean**	**0.2**	**342**	**57**	**471**	**13**	**69**
	SD	0.2	287	46	214	5	17
	Max	0.8	998	149	819	24	97
	Min	<0.5	58	14	75	3	40
POSSERA n = 18	**Mean**	**0.9**	**232**	**64**	**213**	**57**	**127**
	SD	0.6	155	91	101	102	44
	Max	3.2	650	423	419	424	211
	Min	<0.5	68	26	88	11	67
OTHERS n = 9	**Mean**	**0.3**	**461**	**417**	**550**	**14**	**105**
	SD	0.3	233	986	288	7	71
	Max	0.8	848	3045	1006	25	278
	Min	0.1	181	39	143	3	50
NO OPHIOLITE n = 6	**Mean**	**0.4**	**169**	**62**	**144**	**21**	**93**
	SD	0.2	126	66	76	19	73
	Max	0.8	397	169	254	52	221
	Min	0.1	77	8	58	4	25
Samples grain-size <63 mm		*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
CECINA n = 22	**Mean**	**0.2**	**124**	**43**	**186**	**22**	**86**
	SD	0.2	42	24	66	9	22
	Max	0.6	206	118	337	44	123
	Min	<0.5	65	21	102	11	42
POSSERA n = 23	**Mean**	**0.7**	**107**	**60**	**121**	**34**	**138**
	SD	0.2	43	28	61	25	54
	Max	1.3	236	136	321	108	290
	Min	<0.5	58	31	56	15	86
OTHERS n = 10	**Mean**	**0.1**	**91**	**45**	**108**	**23**	**79**
	SD	0.2	59	33	69	14	32
	Max	0.7	232	127	272	50	126
	Min	0.1	19	15	29	12	33
Litological samples		*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
n = 7	**Mean**	**0.5**	**304**	**28**	**303**	**14**	**74**
	SD	0.1	540	7	553	8	15
	Max	0.6	1514	40	1541	30	93
	Min	0.4	42	18	30	5	44

n = number of samples

n = number of samples

Even for Zn, the highest average values are reported in the sediments of Possera Creek for both analyzed grain sizes (average value 127±44 mg/kg for fraction < 2000 µm and 138±54 mg/kg for fraction < 63 µm). The average Zn contents for the Cecina River sediments are 69±17 mg/kg and 86±22 mg/kg for coarse and fine-grained samples, respectively. The sediments sampled along the other streams have average concentration of this metal of 105±71 mg/kg in the coarse fraction and of 79±32 mg/kg in the fine fraction. The samples taken in rivers where the outcrops of ophiolitic rocks are missing have average Zn value 93±73 mg/kg (fraction < 2000 µm). The maximum value of Zn (277.8 mg/kg) for the coarse fraction is found in sample BG 2 of Botrogrande tributary, in which there is also the maximum value of Cu. The fraction < 63 µm has the maximum Zn content of 290 mg/kg in the sample BC03 (Possera Creek), the highest value for this element found in all samples analyzed. The Zn average is 74 mg/kg in samples of the main geological formations (Table 6); the minimum value (44 mg/kg see Table 5) is found in the sample of ophiolitic soil (BC58) and the maximum (93 mg/kg) in the sample of the Neogene "Argille e Gessi del F. Era" (BC52).

Fig. 3 compares Cr and Ni concentration in the fractions < 2000 µm (3a) and in the fractions < 63 µm (3b) of stream sediment samples, collected in several watercourses. These scatter plots also show the value of the two heavy metals analyzed in samples of the main geological formations of the surveyed area, as reported in Table 5. The distribution pattern of the Cr and Ni concentrations follows generally a linear trend in both of the two particle sizes. In addition, some samples < 2000 µm of the lower portion of Cecina River show a deviation from linearity because they have Ni values > 400 mg/kg and Cr < 300 mg/kg (circle in Fig. 3a).

The Cr and Ni contents are > 300 mg/kg in many samples of the coarse fraction (Fig. 3a), especially for stream sediments of Trossa, Rialdo and Sterza Creeks (TR1, RL2 and ST2 samples; values > 700 mg/kg, small box Fig. 3a) but also of Cecina River (BC16, FC9, FC19 and FC20 samples). Samples collected upstream of the river (out of the area affected by the input of ophiolitic rocks) have the lowest values of Cr and Ni (< 100 mg/kg, samples FC1 and BC40). Among the samples taken in the "no Ophiolite" basins, the BC43 has anomalous high values of Cr and Ni compared to the others (397 mg/kg and 203 mg/kg, respectively).

High values of Cr and Ni in the residual soil sample (BC58, small box in Fig. 3a and b) derived from serpentinite outcrops of Montecerboli are observed (Cr 1514 mg/kg and Ni 1541 mg/kg, Table 5). The seven lithological samples have average values of Cr and Ni of 304 mg/kg and 303 mg/kg respectively (Table 6). The concentrations of Cr and Ni found in the two samples of Argille Azzurre (BC39 and BC51) are quite variable, from about 300 mg/kg to 40 mg/kg. The others lithological samples have Cr and Ni abundance ≤ 110 mg/kg (Fig. 3). The Cr and Ni concentrations are < 300 mg/kg (Fig. 3b) in most of the fine fraction samples (< 63 µm); the Ni content slightly exceeds this value only in BC11 (Possera Creek) and F14 sample (Cecina River). In this size fraction Ni shows a slight tendency to enrichment in the stream sediments of Cecina River, which show metal concentration > 200 mg/kg. This is characteristic for samples taken in the lower course of the Cecina River.

The other tributaries have Ni and Cr levels < 150 mg/kg and < 100 mg/kg respectively; only in the sample SA7 of Trossa Creek the Ni and Cr concentrations are higher than these values (271.7 mg/kg and 232.1 mg/kg respectively).

In order to assess the role of grain size on the Cr and Ni distribution and in order to determine the different sources of these two heavy metals, their contents in three particle sizes (< 2000 µm, < 125 µm, < 63 µm) of the stream sediment samples of Possera Creek have been compared. The Cr and Ni values in most stream sediment samples < 2000 µm of Possera Creek (see Fig. 4), except a few samples of the upstream portion of the river, exceed the threshold concentration of contamination ($MCL_{Tab.A}$ in Fig. 4) for sites for residential use ($Cr_{Tab.A}$ = 150 mg/kg and $Ni_{Tab.A}$ = 120 mg/kg) imposed by Italian law (Legislative Decree No. 152/2006). Instead, only a few samples (BC16 and BC18) exceed the threshold concentration of contamination of Cr and Ni ($MCL_{Tab.B}$ in Fig. 4) for commercial and industrial sites ($Cr_{Tab.B}$ = 800 mg/kg and $Ni_{Tab.B}$ 500 mg/kg).

The concentrations of both metals lie below the threshold of concentration for residential sites ($MCL_{Tab.A}$) in the two thinner fractions (< 63 µm and < 125 µm) of Possera Creek samples. Only in some samples, in particular, Ni (Fig. 4 b) exceeds such concentration limit or has a similar value ($Ni_{Tab.A}$ = 120 mg/kg). Moreover, the two thinner grain sizes of Possera Creek stream sediments present a similar concentration trends for both metals.

Statistical data analysis

For a better understanding of the Cr and Ni origin in stream sediments of the investigated area, a multivariate statistical method was applied. The HCA on 6 variables

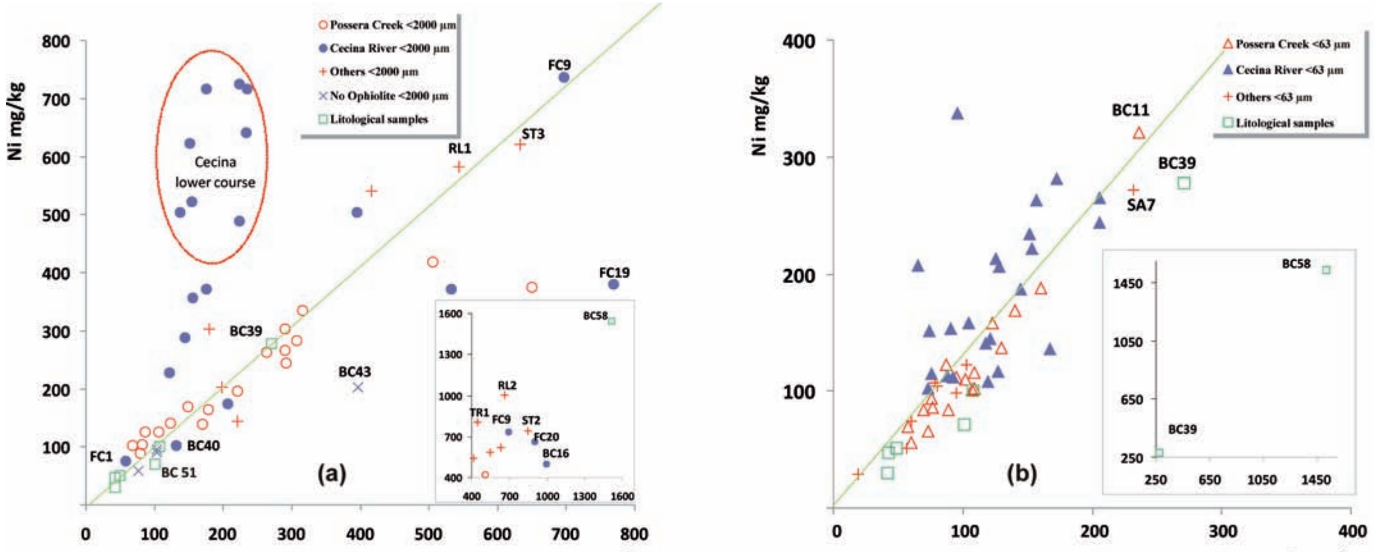


Fig. 3 - Scatter plot of Ni vs Cr concentration (mg/kg) in the stream sediment samples of Cecina River and its tributaries: (a) grain-size < 2000 µm; (b) grain-size < 63 µm. The concentration of two heavy metals in samples of the main geological formations are also shown. The 1:1 relation is shown by the solid line.

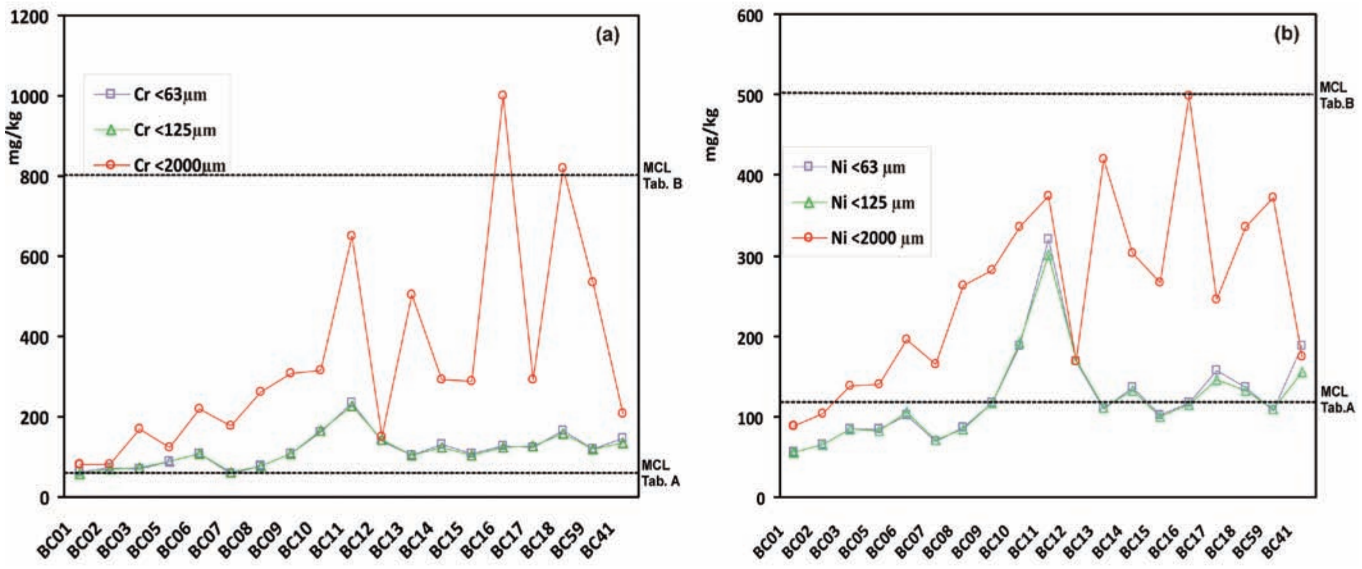
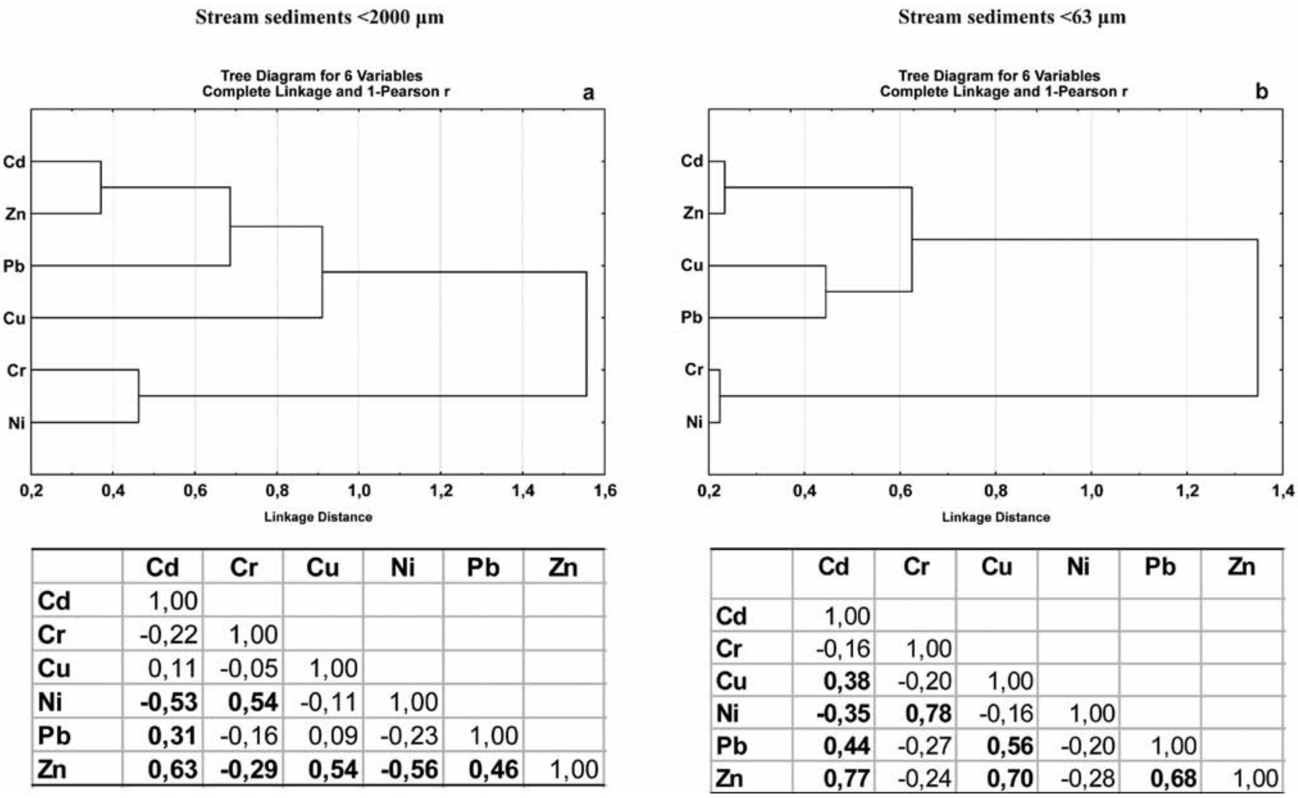


Fig. 4 - Distribution of Cr (a) and Ni (b) in size fraction < 2000 µm and < 63 µm of stream sediment samples of Possera Creek. Dotted lines represent the threshold concentrations of contamination: for residential sites ($MCL_{Tab.A}$) and for commercial and industrial sites ($MCL_{Tab.B}$) (Legislative Decree No. 152/2006, Part IV, Title V, Attachment 5).



	Cd	Cr	Cu	Ni	Pb	Zn
Cd	1,00					
Cr	-0,22	1,00				
Cu	0,11	-0,05	1,00			
Ni	**-0,53**	**0,54**	-0,11	1,00		
Pb	**0,31**	-0,16	0,09	-0,23	1,00	
Zn	**0,63**	**-0,29**	**0,54**	**-0,56**	**0,46**	1,00

	Cd	Cr	Cu	Ni	Pb	Zn
Cd	1,00					
Cr	-0,16	1,00				
Cu	**0,38**	-0,20	1,00			
Ni	**-0,35**	**0,78**	-0,16	1,00		
Pb	**0,44**	-0,27	**0,56**	-0,20	1,00	
Zn	**0,77**	-0,24	**0,70**	-0,28	**0,68**	1,00

Fig. 5 - Dendrogram of heavy metals and Pearson's correlation coefficient matrix for fraction < 2000 µm (a) and for fraction < 63 µm (b) of stream sediment samples (correlations marked in bold are significant at $p < 0.05$).

(Cd, Cu, Cr, Ni, Pb, Zn) in 56 stream sediments < 2000 µm and 49 samples < 63 µm was carried out. Fig. 5 shows the dendrograms of heavy metals analyzed in two grain sizes; Pearson's correlation coefficient matrices among the selected heavy metals in fraction < 2000 µm and < 63 µm in the tables of Fig. 5a and 5b respectively, are presented.

The HCA separates the studied trace metals in two main groups (Cr-Ni and Cd-Zn-Pb-Cu), as well as in coarse-grained samples as in fine-grained sediments. The clustering process points out the association between Cr-Ni in both size fractions but with greater similarity for samples < 63 µm (Linkage Distance < 0.4 in Fig. 5b). This behaviour is also confirmed by the strong Pearson's correlation coefficient between the two elements (r = 0.78).

The second cluster shows a good Cd-Zn association in samples < 2000 µm (r = 0.63) and in samples < 63 µm (r = 0.77). In coarse-grained samples (Fig. 5a), Pb has a single significant correlation but weak with Cd (r = 0.31). Cu does not present a high value of linkage (> 0.8) with the other metals of the cluster. Cu has only one significant correlation

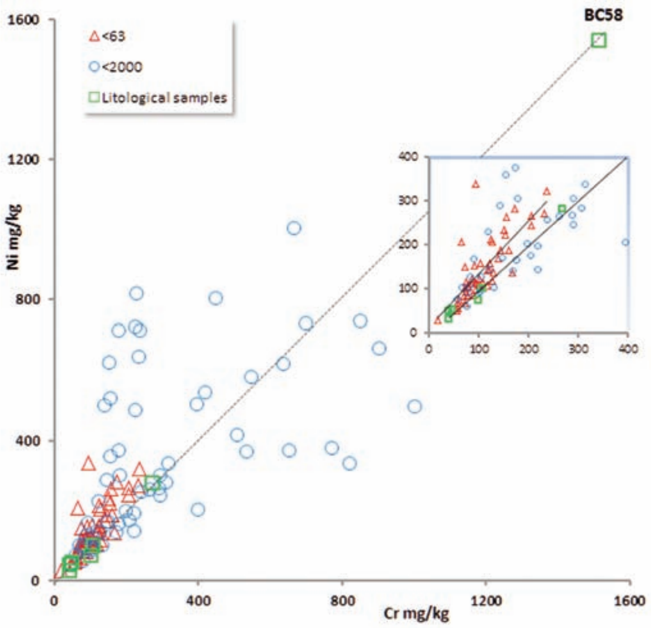


Fig. 6 - Ni vs Cr distribution in all samples from Cecina catchment separated for grain-size (< 2000 µm and < 63 µm). In the small box are shown Cr and Ni concentrations < 400 mg/kg.

with Zn (r = 0.54). Instead, Cu is more strongly associated in the samples < 63 µm with Pb (dendrogram in Fig. 5b) and these two elements have a positive correlation but not strong (r = 0.56) between them. Higher is the correlation Zn-Cu (r = 0.70) and Zn-Pb (r = 0.68).

Petrographic analysis

In Fig. 7 the most representative images of thin sections analyzed are shown.

In all thin sections studied the ophiolite grains represent more than 50% until to reach 80% in the SC6, SC9 and FO1 samples. Due to coastal processes the beach samples (Sm1, Sn and Fm) show good rounded grains as opposed to river samples where the grains are generally more angular. Among the ophiolitic grains, the serpentinite rocks are very well represented with all typical reaction textures where the needle shaped serpentine minerals occur in aggregates interwoven like a mesh or replace the granular primary crystals giving rise to hour-glass like appearances. Textures may be cut by late veins of fibrous serpentine. Serpentinization is almost complete and scarce relicts of primary minerals (olivine, pyroxene, spinel) are observed locally. Some aggregates of serpentine minerals retaining the prismatic shape indicates completely replaced of Opx and Cpx crystals. Olivine is often replaced by a mesh texture formed by growth of serpentine along curved fractures and along grain boundaries, sometimes with hour-glass textures infilling regions in the mesh. The serpentinization of olivine is often accompanied by the formation of iron-oxides heterogeneously distributed within the mesh texture. Serpentine can be anhedral and interstitial to magnetite, and usually encloses fine magnetite crystals forming networks within the serpentinized matrix. Magnetite is especially developed in core rather than rim of individual cells of the mesh-textured serpentine. Also chlorite is a pervasive alteration minerals often matched to serpentine and magnetite. Chromian spinel is always present in anhedral crystals. It is fresh in most instances, although minor alteration to magnetite is present locally.

The textures and mineralogical association observed in thin section are characteristic of serpentinite of harzburgite parentage according to Piccardo et al. (2002).

In addition to the serpentinite grains in thin sections studied varying percentages of other ophiolitic rocks (between 10 to 30 percent) are present. Particularly, we observed abundant intrusive textures related to gabbric rocks and less common basaltic grains with effusive textures. The paragenetic association in gabbroic rocks are anortitic plagioclase and clinopiroxene, often retrocessed to actinolitic anphibole. All Fe-Mg minerals are more or less alterated to chlorite and oxides.

In the thin sections other grains are constituted by sedimentary rocks. Chemical/biogenic constituents are uncommon compared to terrigenous constituents. The latter are represented by sandstones, shales and quarzites.

DISCUSSION

The ophiolite outcrops in the Cecina River basin (total extension of 927 square km, as reported in Table 1) represent 7.6% on the total area of the basin or 15% including Sterza, Trossa, Pavone, Possera, Rialdo and Acquerta sub-basins. The sum of surface of these sub-basins (433 sq. km) represents about half of the whole Cecina River basin.

The extension of the ophiolitic rocks in the Rialdo basin is greater than the others sub-basins (36 % on a total extension of 45 sq. km), which are ordered by extension as follows: Trossa (22.5% on 112 sq. km), Sterza (8.6% on 128 sq. km), Pavone (6.2% on 89 sq. km) and Possera (8.9% on 36 sq. km).

The incidence of serpentines is higher in the basins of Trossa, Rialdo and Pavone Creeks (percentages of serpentinite compared to ophiolite is > 80%). In particular, these rocks have extensive outcrops in the high-middle course of Trossa, Sterza and Rialdo sub-basins (see Fig. 2).

Petrographic analyses of thin sections of stream sediment samples of Cecina River revealed the presence of Cr-rich minerals, as Cr-spinel (Cr-spl), and Cr and Ni-rich minerals as pyroxene (Fig. 7). In addition to these minerals of primary paragenesis, secondary minerals of alteration like serpentine and chlorite, rich in Ni and Cr, have been identified.

The average Cr and Ni concentration (Cr range 307-366 mg/kg and Ni 109-150 mg/kg) in stream sediments of Cecina catchment basin for both analyzed particle sizes exceeds the average abundance of the two heavy metals in upper continental crust (85 mg/kg for Cr and 50 mg/kg for Ni, using X-ray fluorescence analysis method), reported by Taylor and McLennan (1985).

High concentrations of both elements are observed in stream sediments of sub-basins where the ophiolite outcrops are more extensive, especially in the coarse fraction (Fig. 3), but also Cecina River samples show high values.

The highest Cr and Ni values occurred in the samples collected in the Rialdo Creek, near its confluence with the Cecina River, in Trossa and Sterza Creeks (see box in Fig. 3a). Serpentinites are present in the area drained by these tributaries (see Fig. 2). Instead, in the watercourses where the ophiolite outcrops are missing (samples define "no Ophiolite" in Table 2), the sampled sediments do not have meaningful Cr and Ni enrichments, especially in the coarse fraction (Table 2). The presence of Cr-rich minerals, Cr and Ni-rich minerals and other minerals derived from ophiolitic rocks in coarse fractions of Cecina River samples was confirmed by

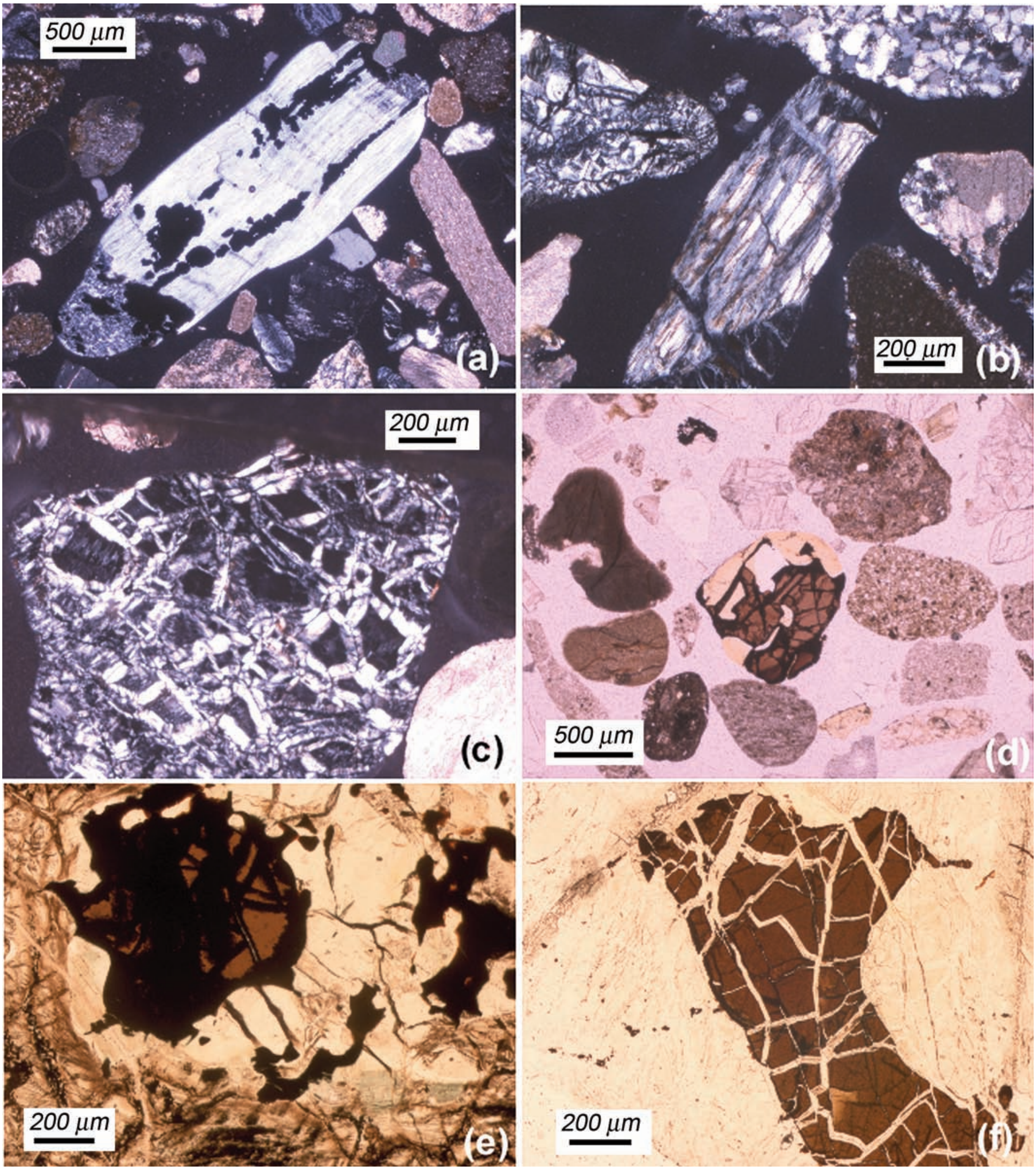


Fig. 7 - Petrographic thin sections of stream and beach sediments samples on grain size ranging from 2000 μm down to 63 μm; PL plane-polarized light; CL cross-polarized light. (a) CL, serpentinization of olivine is accompanied by the formation of iron-oxides heterogeneously distributed within the mesh texture; (b) CL widespread development of the pseudomorphic mesh and bastite texture after orthopyroxenes; (c) CL, serrate chrysotile veins and ribbons of coalesced mesh and hourglass cells; (d) (e) (f) PL, anhedral and fractured crystals of Chromian spinels; in (d) and (e) minor alteration to magnetite is present.

petrographic analyses of thin sections. There is an evident link between high Cr and Ni concentrations in sediments of Cecina River downstream of Rialdo, Trossa and Sterza tributaries and the presence of ophiolite outcrops in the area.

The residual soil sample derived from ophiolitic rocks of Montecerboli (BC58) is the end-member of this data set. This sample shows Cr and Ni contents quite similar to content of residual soil derived from serpentine rocks reported in several studies (Bini et al., 1990; Oze et al., 2003). Cr and Ni-enrichments are therefore associated to the sedimentary contribution of ultramafic lithologies outcropping in the study area.

The highest concentrations of the two elements (> 400 mg/kg) are observed in the coarse grain fraction (< 2000 µm samples) as shown in Fig. 6, where concentration distribution pattern of Cr vs Ni in the two grain sizes analyzed (< 2000 µm and < 63 µm) of stream sediments and in samples of lithology is compared. For concentrations < 400 mg/kg (small box in Fig. 6) there are two different trends. Ni has a tendency to enrichment in fine fraction (< 63µm). Instead, Cr tends to be enriched in the fraction < 2000 µm. The accumulation of greater quantities of fine sediments in low courses of river explains Ni-enrichment in fraction < 63 µm. The lower energies of river flow allow a differentiated selection of coarse sediments enriched in more erosion-resistant minerals. In fact, in the coarse sediments of the study area resistant primary Cr-rich minerals of ophiolitic origin (i.e., Chromite) have been observed. For concentration > 400 mg/kg, Ni is also enriched in fraction < 2000 µm of samples of the lower course of the Cecina River (circle in Fig. 3a). All these differential accumulations could be explained by hydraulic sorting as a function of mineralogical species.

The fine-grained fraction is often used in many studies on heavy metals contamination (Förstner and Salomons, 1980) due to strong association of metals with silt and clay. In general metal concentrations decrease with the increase of the grain size (Salomons, 1980; Groot et al., 1982). In the absence of a natural enrichment, high concentrations of heavy metals in the fine fraction could indicate the presence of anthropogenic inputs. The coarse sediments are more resistant to alteration and erosion by geomorphological agents and they retain the chemical characteristics of source rocks. In Cecina River basin, the weathering of ultramafic rocks, known to produce soils and sediments with high Cr and Ni contents (Brooks, 1987; Schreier et al., 1987; Alexander et al., 1989; Gough et al., 1989; Gasser and Dahlgren, 1994), explains the enrichment of two metals in all size fractions.

Most of the stream sediments of the Cecina River basin exceed the Cr and Ni contamination threshold (Fig. 4) in soils and sediments as imposed by the Italian law (Legislative Decree No. 152/2006) due to enrichments of these two heavy metals associated with serpentine rocks. According to a normal geomorphological evolution of slopes, all the alluvial sediments of the Cecina River basin are probably enriched of Cr and Ni similar to the stream sediments analyzed in this study. These enrichments are evident near the more widespread serpentinite outcrops. The only limited and small outcrop of serpentine rocks in the high portion of Era River catchment explains the Cr and Ni anomalies in the BC43 (Fig. 3a).

Finally, the Cr and Ni levels in the fractions < 63 µm and < 125 µm of Possera Creek samples do not show marked differences of distribution (Fig. 4). This aspect should be considered in order to optimize sampling times and methods. In addition to Cr and Ni, the other elements Cd, Cu, Pb and Zn were investigated in order to discriminate the presence of different heavy metals sources, including the non natural ones.

Cd has high values in all samples (< 2000 µm and < 63 µm) near the industrial area of Larderello (maximum values in BC03 sample). In this area high concentrations of Cu, Pb and Zn are also observed in both analyzed size fractions. High Cu contents in Botrogrande Creek (BG1, BG2, SA5, SM4) are due to mining of mixed sulphide mineralization of Montecatini Val di Cecina, one of the most important copper mines exploited during the 18th and 19th century (Fig. 1a), located upstream of the sampling point. This also explains the Cu levels (40 mg/kg) founded in the Argille Azzurre sample (BC39). High Cu values are also observed in some samples < 2000 µm in the lower course of Cecina River, collected upstream of the mouth (from FC16 to FC19). This behaviour is like the one observed for Ni and Cr. The sample SM2 has high values of both Cu, Cd, Zn and Pb and was taken immediately downstream of a chemical industry. This could indicate the presence of a non-natural source of these heavy metals in the investigated area. High levels of these metals are also reported in BC06 (Possera Creek), sampled near Montecerboli, downstream of Larderello. In this sample are also found high Cr and Ni contents. Two heavy metals sources might therefore be supposed: a natural one for Cr and Ni given the presence of serpentinite outcrops of Montecerboli near the sampling point; while the other one probably has an anthropogenic origin. This explains the high Cd, Cu, Pb and Zn values, not highlighted in the representative sample of the natural source (BC58).

Moreover, the Hierarchical Clustering Analysis carries out a clear distinction between Cr and Ni strongly associated and the other analyzed heavy metals. Cr and Ni have a specific source that is different from the source of Cd, Cu, Pb and Zn. The association Cu-Pb, Zn-Cu and Zn-Pb suggests the existence of a unique source of these elements. This source can be the mixed sulphide mineralization scattered in the study area. The high levels of some metals (Cu, Pb, Zn and Cd) in the fine fraction of the stretch of the Possera Creek near the Larderello industrial site (Fig. 1b) indicate the presence of other types of sources of heavy metals in this area probably due to anthropogenic activities.

CONCLUSIONS

This study has allowed to determine Cr and Ni levels in stream sediments of Cecina River and some its tributaries and their spatial distribution. The results show a natural geochemical anomaly of Cr and Ni in the Cecina River basin linked to the presence of ophiolitic rocks. The highest concentrations are found in the parts of watercourse affected by the contribution of serpentinite outcrops. In fact, the study showed that the highest concentrations come from the tributaries where outcrops of serpentinite rocks are more extensive. Cr and Ni-enrichment is therefore associated with sedimentary contribution of ultramafic lithologies outcrops located in the study area.

This is further confirmed by comparing the Cr and Ni values in different grain size fractions of stream sediments. The coarser fraction (< 2000 µm) shows a greater enrichment than the fraction < 63 µm because coarser fraction retains the chemical characteristics of serpentinized ultramafic rocks. Petrographic analyses have identified minerals rich in Cr and Ni (as Cr-spinel and Cr/Ni-rich pyroxene) in the coarse fractions of samples.

This study allowed to demonstrate that the distribution of trace elements depends on the nature of the source. In this case, Cr and Ni are closely associated with the mineral fractions produced by weathering of ophiolitic rocks.

Although of natural origin, high concentrations of these elements affect sediment quality of the Cecina River basin. In fact, the Cr and Ni levels often exceed the Italian law limit values (Legislative Decree No. 152/2006). According to a normal geomorphological evolution of slopes, all the alluvial sediments of the Cecina River basin may have the same critical environmental problem. It would be useful to assess possible release into the environment of these elements by sequential extraction procedures and toxicity testing.

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